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(54) COMPOSITE CERAMIC MATERIAL AND METHOD TO MANUFACTURE THE MATERIAL

KOMPOSIT-KERAMISCHES MATERIAL UND VERFAHREN ZUR HERSTELLUNG

MATIERE CERAMIQUE COMPOSITE, ET PROCEDE DE FABRICATION

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- **CHEMICAL ABSTRACTS, Volume 108, No. 2, 11 January 1988, (Columbus, Ohio, US), see page 336, Abstract 11277v, & JP,, 62142565**
- **DERWENT'S ABSTRACT No 87-281769/40, JP 62197066, publ.week 8740, Dialog Information Service, File 351, WPI.**

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The file contains technical information submitted after the application was filed and not included in this specification

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Description

TECHNICAL FIELD

The present invention relates to a method to manufacture a composite ceramic material having a high strength combined with bioactive properties when the material is used as a dental or orthopedic implant. The invention relates also to a method to manufacture the composite ceramic material.

BACKGROUND ART

Ceramic materials and particularly structural ceramic materials generally have a high resistance to corrosion and erosion. This is true of e.g. several oxides, nitrides, carbides and borides. Also, said materials have no toxic properties. When used as implant materials said materials are completely inactive, i.e. neither positive nor negative reactions with surrounding tissues take place, and consequently it is possible to attain a biological integration to bone tissue without any intermediate connective tissue. Such materials are termed inert when used as implant materials. These properties make several oxides, nitrides, carbides and borides potentially very valuable as inert dental and orthopedic implant materials.

However, it is desirable that materials having a favourable biocompatibility are not only inert, i.e. able to fasten mechanically to a bone tissue, but also bioactive, i.e. the implant can be bonded chemically to a bone tissue. Oxides, nitrides, carbides and borides do not have this property. On the other hand it is known that phosphate-based materials, having a chemical composition similar to the "inorganic" or "ceramic" matter in bone tissue, can display bioactive properties. Such a phosphate-based material is e.g. hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$. However, a synthetic hydroxylapatite has a low tensile toughness and hence a low strength and also a tendency to gradually develop a continuous crack growth. Another example of a bioactive material having a calcium phosphate-base is tricalcium phosphate $Ca_3(PO_4)_2$, but this compound has an unsatisfactory strength. Also, it has a not negligible water solubility and consequently may be dissolved before the bond to the bone tissue has developed. Thus, in this respect, hydroxylpatite is preferred as compared to tricalcium phosphate.

DE-A- 3301122 deals with the manufacture of an implant material of 70-95 weight percent TiO_2, with balance being hydroxylapatite powder, the mixture being precompressed and subjected to sintering.

Chemical Abstracts 108 : 11277V briefly describes the manufacture of ceramic implant material from zirconium oxide and calcium phosphate which are mixed and sintered at a temperature between 1100°C and 1500°C. Specifically it mentions hot pressing at 1350°C and 200 kg/cm^2 which corresponds to about 20 MPa.

BRIEF DISCLOSURE OF THE INVENTION

The object of the invention is to suggest a composite ceramic material having a so called duo-quality, i.e. a high strength combined with a bioactivity, when the material is used as a dental or orthopedic implant. This and other objects can be attained by a material, essentially constiting of at least one oxide belonging to the group consisting of titanium dioxide (TiO_2), zirconium oxide (ZrO_2) and aluminum oxide (Al_2O_3), and at least one of hydroxylapatite and tricalcium phosphate, and said material having a structure obtainable by preparing a powder mixture, mainly consisting of a first powder consisting of at least one oxide belonging to the group consisting of titanium dioxide (TiO_2), zirconium oxide (ZrO_2), and aluminum oxide (Al_2O_3), said at least one of hydroxylapatite and tricalcium phosphate being included in an amount of 5-35, preferably 10-25 percent by volume, making a raw compact of the prepared powder mixture, and densifying said raw compact to at least 97 % of the theoretical maximum density, i.e. of its full density through an isostatic pressing of the raw compact in a hot condition (HIP) at a pressure of at least 150 MPa but not more than 250 MPa and at a temperature of 900-1300°C, wherein the phosphate will exist as particles in a matrix consisting of said at least one oxide, the maximum mean distance between the calcium phosphate particles being 5µm, preferably 2µm.

The used hydroxylapatite can be entirely synthetic or consist of a bone ash, which also contains other compounds than hydroxylapatite in small contents.

The material is produced by preparing a powder mixture, mainly consisting partly of a first powder, which as to its chemical state is designed to constitute a bioinert matrix in the finished material, and partly of a second powder mainly consisting of a calcium phosphate-based material, wherein the first powder comprises at least one oxide belonging to the group consisting of titanium dioxide (TiO_2), zirconium oxide (ZrO_2) and aluminum oxide (Al_2O_3); the second powder mainly comprises at least one of hydroxylapatite and tricalcium phosphate; a raw compact is made of the powder mixture, and said raw compact is densified to at least 97 % of the theoretical maximum density, i.e. of its full density through an isostatic pressing in a hot condition (HIP) at a pressure of at least 150 MPa and not more than 250 MPa and at a temperature of 900-1300°C, a composite material being obtained, in which the matrix comprises one or several metal oxides of said first powder, in which matrix said hydroxylapatite and/or tricalcium phosphate are evenly dispersed, and

wherein said powder mixture is composed in such a way, that said composite ceramic material will comprise 5-35, preferably 10-25 percent by volume of said hydroxylapatite and/or tricalcium phosphate.

The comparatively low sintering temperature is advantageous, e.g. for the following reasons:

- The grain growth is limited, which favours a high strength;
- A decomposition of the calcium phosphate material (hydroxylapatite or the like) is avoided or limited to an acceptable extent; and
- Undesirable reactions between oxides, e.g. titanium dioxide, and the calcium phosphates are prevented.

When the powder material is consolidated, no chemical reactions take place. The powder mixture suitably is composed in such a manner, that the calcium phosphate-phase will appear as small islands, i.e. as discrete particles, in the matrix, which according to the invention consists of one or several oxides belonging to the group, which comprises titanium dioxide, zirconium oxide and aluminum oxide. One might expect that 5-35 percent by volume of calcium phosphate material in the inert matrix is not sufficient to ensure the desired bioactivity but at the same time will result in a risk of a substantial deterioration of the strength properties. However, we have found that these fears are groundless. Thus, clinical experiments, performed on living animals, have shown, that the material according to the invention has a bioactivity, which is entirely comparable to the bioactivity of pure hydroxylapatite. Thus, it is not necessary to coat the inert matrix with pure hydroxylapatite in order to obtain the desirable bioactivity, which otherwise is customary according to known practice. However, the admixture of calcium phosphate material into the matrix probably must be very finely dispersed and even in order to obtain a very large number of islands per exposed surface unit, the distance between adjacent islands of calcium phosphate at the same time being very small. These conditions probably will facilitate the addition of a new bone tissue, but the causal relations have not been completely explained. The very finely dispersed and even nature of the distribution of the calcium phosphate fraction in the matrix can also explain the retained very high strength. Thus, provided one regard the calcium phosphate particles as defects of the matrix, it is possible to calculate the largest possible size of the calcium phosphate islands in different oxide materials in order to obtain a certain so called critical intensity factor (critical toughness), known for the matrix. Thus, if the matrix is tougher, the islands can be larger than in a brittle matrix and vice versa. These theoretical considerations and practical results lead to the following recommendations for a composite consolidated material consisting of a matrix, which comprises metal oxides, and a calcium phosphate material dispersed in the matrix, preferably hydroxylapatite.

Matrix	Maximum size of the calcium phosphate particles	Mean distance between the calcium phosphate particles
TiO_2	10 µm	max 5 µm, pref. max 2 µm
Al_2O_3	15 µm	"-
ZrO_2	30 µm	"-

Thus, as regards the strength, zirconium oxide is preferred to aluminum oxide, which in its turn is better than titanium dioxide. Also, the oxides differ as to their chemical resistance. Thus, whereas the temperature during the hot isostatic pressing should not be higher than 1000°C, when the matrix is composed of titanium dioxide, it can be as high as 1300°C and preferably 1100-1250°C, when a matrix of aluminum oxide and/or zirconium oxide is used.

Whereas according to known practice one believes that it is necessary to provide an implant with a coat, which entirely consists of a bioactive material, which means that in certain cases the implant has been provided with an outer coat of a calcium phosphate material, according to the present invention it is possible to use the duo-properties of the composite material according to the invention, an extra outer coat of hydroxylapatite or the like then not being necessary. However, it is also, within the scope of the present invention, possible per se to cover a "duo-material", completely or partially, with layers of materials having another composition or to produce implants, in which different parts have different compositions, including at least one part consisting of a composite material according to the invention having duo-properties and at least one part consisting of a homogenous material, e.g. a ceramic material without any admixture of a calcium phosphate material or an entirely metallic material. These and other aspects of the invention are also set forth in the patent claims and will be further elucidated in the following description of a few preferred embodiments.

BRIEF DESCRIPTION OF DRAWINGS

The invention will now be explained in more detail by means of a few illustrative examples and experiments carried out, reference being made to the accompanying drawings, in which:

Fig. 1 shows a microstructure of a material according to a first preferred embodiment according to the invention;

Fig. 2 is a drawn picture, based on an X-ray photograph, which shows how an implant according to the invention has adhered to a natural bone material;

Fig. 3 shows a longitudinal section of a product according to a possible embodiment of the invention;

Fig. 4 shows a longitudinal section of a product according to another possible embodiment of the invention; and

Fig. 5 shows a longitudinal section of a product according to an additional possible embodiment of the invention.

DESCRIPTION OF EXPERIMENTS CARRIED OUT AND EMBODIMENTS

Raw materials used in the trials are listed in Table 1. Monolithic materials (titanium dioxide and hydroxylapatite respectively) as well as composite materials (combinations of oxides and calcium phosphate materials), Table 2, were produced from powders of these raw material. The powder mixtures and a silicon nitride grinding agent in petroleum ether were admixed in a ball mill and were ground for 20 h. Subsequent to an evaporation in an evaporator raw compacts were produced from the powder mixtures by a cold isostatic compacting (CIP) at a pressure of 300 MPa. The raw compacts thus obtained were encased in glass and densified by a hot isostatic pressing (HIP) at a pressure of 200 MPa for 1 h at a maximum temperature of 925°C for the TiO_2-based materials and at 1225°C for the other materials. Subsequent to the densification the materials displayed a density of more than 99% of the theoretical maximum density. The HIP-temperatures and the obtained densities are also shown in Table 2.

Table 1

- Raw material	
Designation	Description
BA	Hydroxylapatite of bone ash
HA	Hydroxylapatite, grade Merck
TCP	β-tricalcium phosphate, grade Merck
A	α-aluminum oxide, AKP-30, Sumitomo
R	Titanium dioxide, Tioxide Ltd
Z	Zirconium dioxide (including 3 mol-% Y_2O_3)

Table 2

- Powder mixtures which have been compacted by a hot isostatic pressing; densities of HIP-produced specimens				
Specimen No.	Powder, % by volume	HIP-temp., °C	Density g/cm^3	
			Recorded	Theoretical
1	70HA/30A	1225	3.39	3.40
2	25HA/75A	1225	3.75	3.77
3	15BA/85A	1225	3.85	3.85
4	15HA/85R	925	4.02	4.09
5	7.5TCP/7.5HA/85A	1225	3.77	3.85
6	7.5TCP/7.5HA/85R	925	4.04	4.09
7	15HA/85Z	1225	5.64	5.65

Table 3

Specimen	Tensile strength (MPa)	Weibull-module (m)	Toughness ($MPam^{1/2}$)	Hardness (5N) (GPa)
HA	110	18	1.1 ± 0.1	3.9 ± 0.3
1	250	n.d.*	2.0	7.1
2	535	n.d.*	4.0	20.2
3	601	19	3.5	18.9
4	252	9	2.9	8.4
5	446	10	3.4	17.8
6	397	n.d.*	2.6	10.9
7	820	n.d.*	>7	13
A	400-560	-	4	22
R	405	10	-	12
Z	980	n.d.*	>7	14

* not measured

Test bars were made with the size 3x3x30 mm. The test bars were examined in a three-point test to measure the compressive strength in bending. The Weibull-modules were measured. The toughness was measured using Vicker's indentation depth-method, as well as the hardness at a load of 10 N and 5 N respectively. Some specimens were etched for 20 seconds in a 0.1 % HF-solution in order to study the microstructure in SEM.

In order to study the bioactive properties of the materials cylinders were made with a diameter of 3.1 mm and a length of 7 mm. Identical specimens of pure aluminum oxide (negative control) and pure hydroxylapatite (positive control) were also made to be used as reference materials. The implants were inserted by operation in a large hole (3.2 mm diameter) in lateral cortex in rabbits (femorarabbit from New Zealand). After a healing period of three months the animals were put to death and the implants were examined by X-ray radiography, subsequent to the removal of surrounding soft tissue.

Fig. 1 shows the microstructure of a material according to the invention, being composed of 15 percent by volume hydroxylapatite, the remainder being aluminum oxide (specimen 3). The hydroxylapatite-phase is evenly distributed throughout the aluminum oxide-matrix, in which the hydroxylapatite forms particles (grains) or islands (insulets) having a maximum length of < 6 µm. The specimen is somewhat overetched in Fig. 1 in order to be able to identify the microstructure more easily. Some of the smallest grains can be pores. An X-ray diffraction analysis showed that no phase alterations had taken place during the HIP-treatment.

The mechanical properties are shown in Table 3. As is expected, the aluminum oxide-based duo-ceramic materials, specimens 1, 2, 3 and 5, are stronger than the titanium dioxide-based materials, specimens 4 and 6. The strength level of the aluminum oxide-based duo-ceramic material is comparable to the strength level of commercial dental implants made of polycrystalline aluminum oxide, which is 400-560 MPa. The tensile strength is also comparable. The zirconium oxide-based duo-ceramic materials have the highest strength and tensile strength. The results show, that the duo-ceramic materials according to the present invention can be used for dental implants, at least as regards the mechanical properties. This is particularly true of those duo-ceramic materials according to the invention, which are based on aluminum oxide and zirconium oxide, but also the titanium-based duo-ceramic materials in all likelihood can be used as implants, at least in those instances when the mechanical properties are a critical factor.

Fig. 2 shows in a drawing, based on an X-ray radiograph a ceramic cylinder, made of specimen No. 3 in Table 3 and inserted by operation. A new cortical bone material has grown towards the implant (at a) as well as along the surface of the implant (at b). The pattern of bone growth for the duo-ceramic material according to the invention is mainly identical with that for pure hydroxylapatite, as was shown in a comparison test. A similar pattern was also obtained with specimens Nos. 4 and 7, which had a matrix of titanium dioxide and zirconium oxide respectively.

These trials show, that bioactive ceramic materials having a high strength can be produced by means of a hot isostatic pressing of a raw compact, which is composed of at least two powder fractions, a bioactive phase being obtained, which consists of hydroxylapatite and is evenly distributed in an oxidic matrix, which gives the material the required strength. The bioactive phase appears as distinct points, the size of which can be allowed to vary depending on the strength of the matrix, but the mean distance between adjacent points must be smaller than 5 μm, preferably smaller than 2 μm.

In the description above for the invention it has been mentioned that it, within the scope of the inventive concept, also is possible to produce compacts (bodies), in which different parts have different compositions. This will now be illustrated by means of a few possible examples. According to a first embodiment of this aspect of the invention 15 percent by volume hydroxylapatite powder and 85 percent by volume zirconium oxide powder are mixed. The powder is prepared in the same manner as is explained in the description above of experiments carried out. The powder mixture is poured into a polymer can to fill the can up to half its height. Pure aluminum oxide without any admixture of any substance is then added to fill the can completely. The can is closed and the powder is isostaticly compressed in a cold condition at 300 MPa. The compact specimen is then isostaticly compressed in a hot condition at 1225°C for 1 h and at a pressure of 160 MPa. The compact specimen is cut into test bars, in which the center line roughly corresponds to the boundary between pure aluminum oxide and the aluminum oxide/hydroxylapatite-mixture. The test bars (7 of them) with the dimensions 35x3x3 mm are examined using a three-point-bend-testing method. A mean value of the tensile strength was measured to 720 MPa (the lowest value was 540 MPa and the highest 810 MPa).

It is also possible to produce a material similar to the previous one by producing two separate raw compacts, one of them consisting of a powder mixture of a calcium phosphate powder and an oxidic powder and the other one solely consisting of an oxidic powder, and combining the raw compacts through a common isostatic compacting in a hot condition. Fig. 3 shows schematically an example of a work piece produced in this way, in which the joint-ball can consist of a ceramic substance made of pure oxide and the stem can consist of a duo-ceramic substance according to the invention.

Fig. 4 shows schematically another example. In this instance a pure oxidic powder 1 is coated with a duo-ceramic powder 2, powder 2 being partially covering powder 1, subsequent to which the combined powder is isostaticly compressed in a cold condition and after that is encased and isostaticly compressed in a hot condition.

Fig. 5 shows the opposite instance, namely that a raw compact 3 of a duo-ceramic powder according to the invention partially is coated with an oxidic powder 4, before the compact is consolidated through a combined isostatic pressing in a cold condition followed by an isostatic pressing in a hot condition.

A compact of a duo-ceramic material according to the invention can also be treated in order to remove the bioactive phase in the surface area of a section of the component. This can be done through a chemical dissolving of the calcium phosphate phase in the surface layer or through blasting. In either case small cavities are obtained in those areas where the phosphate material previously was present and these cavities can function as liquid reservoirs, in case implants for joints are to be produced. Thus, a certain amount of liquid can be kept and in this way the friction can be reduced within those areas, where a sliding is to take place in the joint. Of course, the remaining parts of the duo-ceramic work-piece are to be left intact in order to be able to utilize the bioactive properties of the duo-ceramic work-piece, where this property is desirable.

Claims

1. Method to manufacture a composite ceramic material having a high strength combined with bioactive properties, when the material is used as a dental or orthopedic implant, which comprises preparing a powder mixture, mainly consisting partly of a first powder, which as to its chemical state is designed to constitute a bioinert matrix in the finished material, and partly of a second powder mainly consisting of a calcium phosphate-based material, wherein the first powder comprises at least one oxide belonging to the group consisting of titanium dioxide (TiO_2), zirconium oxide (ZrO_2) and aluminum oxide (Al_2O_3); the second powder mainly comprises at least one of hydroxylapatite and tricalcium phosphate; a raw compact is made of the powder mixture, and said raw compact is densified to at least 97 % of the theoretical maximum density, i.e. of its full density through an isostatic pressing in a hot condition (HIP) at a pressure of at least 150 MPa and not more than 250 MPa and at a temperature of 900-1300°C, a composite material being obtained, in which the matrix comprises one or several metal oxides of said first powder, in which matrix said hydroxylapatite and/or tricalcium phosphate are evenly dispersed, and wherein said powder mixture is composed in such a way, that said composite ceramic material will comprise 5-35, preferably 10-25 percent by volume of said hydroxylapatite and/or tricalcium phosphate.

2. Method according to claim 1, **characterized** in that said first powder mainly comprises titanium dioxide and in that said raw compact is densified through an isostatic pressing in a hot condition at a temperature of 900-1000°C.

3. Method according to claim 1, **characterized** in that said first powder mainly comprises aluminum oxide and/or zirconium oxide and in that said raw compact is densified through an isostatic pressing in a hot condition at a temperature of 1100-1250°C.

4. Composite ceramic material having a high strength combined with bioactive properties, when the material is used as a dental or orthopedic implant, said material essentially consisting of at least one oxide belonging to the group consisting of titanium dioxide (TiO_2), zirconium oxide (ZrO_2) and aluminum oxide (Al_2O_3), and at least one of hydroxylapatite and tricalcium phosphate, and said material having a structure obtainable by preparing a powder mixture, mainly consisting of a first powder consisting of at least one oxide belonging to the group consisting of titanium dioxide (TiO_2), zirkonium oxide (ZrO_2), and aluminum oxide (Al_2O_3), said at least one of hydroxylapatite and tricalcium phosphate being included in an amount of 5-35, preferably 10-25 percent by volume, making a raw compact of the prepared powder mixture, and densifying said raw compact to at least 97 % of the theoretical maximum density, i.e. of its full density through an isostatic pressing of the raw compact in a hot condition (HIP) at a pressure of at least 150 MPa but not more than 250 MPa and at a temperature of 900-1300°C, wherein the phosphate will exist as particles in a matrix consisting of said at least one oxide, the maximum mean distance between the calcium phosphate particles being 5 µm, preferably 2 µm.

5. Material according to claim 4, **characterized** in that it has a matrix which mainly comprises zirconium oxide, and that the calcium phosphate exists as particles in said matrix, said particles having a maximum size of 30 µm.

6. Material according to claim 4, **characterized** in that it has a matrix which mainly comprises aluminum oxide, and that the calcium phosphate exists as particles in said matrix, said particles having a maximum size of 15 µm.

7. Material according to claim 4, **characterized** in that it has a matrix which mainly comprises titanium oxide, and that the calcium phosphate exists as particles in said matrix, said particles having a maximum size of 10 µm.

8. Body only partially made of a material according to any of claims 4-7, which material forms one of several parts of said body, **characterized** in that one or several other parts of said body mainly are made of one or several of the oxides titanium dioxide (TiO_2), zirconium oxide (ZrO_2) and aluminum oxide (Al_2O_3).

Patentansprüche

1. Verfahren zur Herstellung eines keramischen Verbundmaterials mit hoher Festigkeit in Verbindung mit bioaktiven Eigenschaften bei Verwendung des Materials für ein zahnärztliches oder als orthopädisches Implantat, das die Herstellung einer Pulvermischung beinhaltet, die hauptsächlich zum Teil aus einem ersten Pulver besteht, das von seinen chemischen Eigenschaften her zur Ausbildung einer bioinerten Matrix im fertigen Material geeignet ist, und zum Teil aus einem zweiten Pulver, das hauptsächlich aus einem Material auf Basis von Calciumphosphat besteht, wobei das erste Pulver mindestens ein Oxid beinhaltet, das zu der Gruppe bestehend aus Titandioxid (TiO_2), Zirkonoxid (ZrO_2) und Aluminiumoxid (Al_2O_3) gehört, und das zweite Pulver hauptsächlich aus Hydroxylapatit und/oder Tricalciumphosphat besteht, wobei ein Rohpreßling aus der Pulvermischung hergestellt und der genannte Rohpreßling auf eine Dichte von mindestens 97% der maximalen theoretischen Dichte verdichtet wird, d.h. seiner durch isostatischen Druck unter Heißbedingungen (HIP) bei einem Druck von mindestens 150 MPa und nicht mehr als 250 MPa und bei einer Temperatur von 900°C bis 1300°C erreichbaren vollständigen Dichte, wobei man einen Verbundwerkstoff erhält, in dem die Matrix ein oder mehrere Metalloxide des ersten Pulvers beinhaltet, in dessen Matrix das genannte Hydroxylapatit und/oder Tricalciumphosphat gleichmäßig verteilt ist, und bei dem die genannte Pulvermischung derart zusammengesetzt ist, das der genannte keramische Verbundwerkstoff 5 bis 35, bevorzugt 10 bis 25 Vol. % des genannten Hydroxylapatits und/oder Tricalciumphosphats beinhaltet.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das genannte erste Pulver hauptsächlich Titandioxid beinhaltet und dadurch, daß der Rohpreßling durch isostatischen Druck bei Heißbedingungen bei einer Temperatur von 900°C bis 1000°C verdichtet wird.

3. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das genannte erste Pulver hauptsächlich Aluminiumoxid und/oder Zirkonoxid beinhaltet, und daß der genannte Rohpreßling durch isostatischen Druck bei Heißbedingungen bei einer Temperatur von 1100°C bis 1250°C verdichtet wird.

4. Keramisches Verbundmaterial mit hoher Festigkeit in Verbindung mit bioaktiven Eigenschaften bei Verwendung

des Materials als zahnärztliches oder als orthopädisches Implantat, wobei das genannte Material notwendigerweise mindestens Oxid beinhaltet, das zu der Gruppe bestehend aus Titandioxid (TiO_2), Zirkonoxid (ZrO_2) und Aluminiumoxid (Al_2O_3) gehört, und aus Hydroxylapatit und/oder Tricalciumphosphat, wobei das genannte Material eine Struktur besitzt, die durch Herstellung einer Pulvermischung erhalten werden kann, die hauptsächlich aus einem ersten Pulver besteht, das mindestens ein Oxid beinhaltet, das zu der Gruppe bestehend aus Titandioxid (TiO_2), Zirkonoxid (ZrO_2) und Aluminiumoxid (Al_2O_3) gehört, und der genannte Hydroxylapatit und/oder Tricalciumphosphat in einer Menge von 5 bis 35, vorzugsweise 10 bis 25 Vol.-% darin eingeschlossen ist, wobei ein Rohpreßling aus der hergestellten Pulvermischung hergestellt werden kann und dieser Rohpreßling auf mindestens 97% der theoretischen maximalen Dichte verdichtet werden kann, d.h. auf die vollständige Dichte des Rohpreßlings durch isostatischen Druck unter Heißbedingungen (HIP) bei einem Druck von mindestens 150 MPA, aber nicht mehr als 250 MPa und bei einer Temperatur von 900°C bis 1300°C, wobei das Phosphat als Partikel in einer Matrix, bestehend aus mindestens einem genannten Oxid vorliegt, und der maximale mittlere Abstand zwischen den Calciumphosphatteilchen 5µm, vorzugsweise 2µm beträgt.

5. Ein Material gemäß Anspruch 4, dadurch gekennzeichnet, daß es eine Matrix besitzt, die hauptsächlich Zirkonoxid beinhaltet, und daß das Calciumphosphat als Partikel in der genannten Matrix vorliegt, wobei die genannten Teilchen eine maximale Größe von 30µm besitzen.

6. Ein Material gemäß Anspruch 4, dadurch gekennzeichnet, daß es eine Matrix besitzt, die hauptsächlich Aluminiumoxid beinhaltet, und daß das Calciumphosphat als Partikel in der genannten Matrix vorliegt, wobei diese Teilchen eine maximale Größe von 15µm besitzen.

7. Ein Material gemäß Anspruch 4, dadurch gekennzeichnet, daß es eine Matrix hat, die hauptsächlich Titanoxid beinhaltet, und daß das Calciumphosphat als Partikel in der genannten Matrix vorliegt, wobei die genannten Teilchen eine maximale Größe von 10µm besitzen.

8. Ein Körper, der nur teilweise aus einem Material gemäß einem der Ansprüche 4 bis 7 hergestellt ist, und das eines von mehreren Teilen des genannten Körpers bildet, dadurch gekennzeichnet, daß ein Teil oder mehrere Teile des genannten Körpers aus einem oder mehreren der Oxide Titandioxid (TiO_2), Zirkonoxid (ZrO_2) und Aluminiumoxid (Al_2O_3) bestehen.

Revendications

1. Procédé pour fabriquer un matériau céramique composite ayant une grande résistance mécanique en combinaison avec des propriétés bioactives, quand le matériau est utilisé comme implant dentaire ou orthopédique qui consiste à préparer un mélange de poudres, constitué essentiellement en partie d'une première poudre, qui pour ce qui est de son état chimique est destinée à constituer une matrice bio-inerte dans le matériau fini et e n partie d'une deuxième poudre constituée essentiellement d'un matériau à base de phosphate de calcium, où la première poudre comprend au moins un oxyde appartenant à l'ensemble comprenant le dioxyde de titane (TiO_2), l'oxyde de zirconium (ZrO_2) et l'oxyde d'aluminium (Al_2O_3) ; la deuxième poudre comprend essentiellement au moins l'un des composés hydroxylapatite et phosphate tricalcique ; on prépare un comprimé cru à partir du mélange de poudres et ledit comprimé cru est densifié à au moins 97 % de sa masse volumique maximale théorique, c'est-à-dire de sa masse volumique à plein, par compression isostatique à chaud (HIP) sous une pression d'au moins 150 MPa et non supérieure à 250 MPa, à une température de 900 à 1300°C, ce qui permet d'obtenir un matériau composite, où la matrice comprend un ou plusieurs oxydes métalliques de ladite première poudre, matrice dans laquelle ledit hydroxylapatite et/ou phosphate tricalcique sont uniformément dispersés, et où ledit mélange de poudres est constitué de telle sorte que ledit matériau céramique composite comprenne de 5 à 35 et, de préférence de 10 à 25 % en volume dudit hydroxylapatite et/ou phosphate tricalcique.

2. Procédé selon la revendication 1, caractérisé en ce que ladite première poudre comprend essentiellement du dioxyde de titane, et que ledit comprimé cru est densifié par compression isostatique à chaud à une température de 900 à 1000°C.

3. Procédé selon la revendication 1, caractérisé en ce que ladite première poudre comprend essentiellement de l'oxyde d'aluminium et/ou de l'oxyde de zirconium, et en ce que ledit comprimé cru est densifié par compression isostatique à chaud à une température de 1100 à 1250°C.

4. Matériau céramique composite ayant une grande résistance mécanique en combinaison avec des propriétés bioactives, quand le matériau est utilisé comme implant dentaire ou orthopédique, ce matériau étant essentiellement constitué d'au moins un oxyde appartenant à l'ensemble comprenant le dioxyde de titane (TiO_2), l'oxyde de zirconium (ZrO_2) et l'oxyde d'aluminium (Al_2O_3), et le dit matériau ayant une structure obtenue en préparant un mélange de poudres constitué essentiellement d'une première poudre consistant en au moins un oxyde appartenant au groupe qui comprend le dioxyde de titane (TiO_2), l'oxyde de zirconium (ZrO_2) et l'oxyde l'aluminium (Al_2O_3), ledit au moins un composé hydroxylapatite et phosphate tricalcique étant incorporé en une quantité de 5 à 35 et, de préférence, de 10 à 25 % en volume, en produisant un comprimé cru du mélange en poudre ainsi préparé, ledit comprimé cru étant densifié à au moins 97 % de la masse volumique maximale théorique, c'est-à-dire de sa masse volumique à plein obtenue par une compression isostatique du comprimé cru à chaud (HIP) sous une pression d'au moins 150 MPa mais non supérieure à 250 MPa et à une température de 900 à 1300°C, où le phosphate existe sous forme de particules dans une matrice constituée d'au moins un oxyde, la distance moyenne maximale entre les particules de phosphate de calcium étant de 5 µm et de préférence de 2 µm.

5. Matériau selon la revendication 4, caractérisé en ce qu'il a une matrice qui comprend essentiellement de l'oxyde de zirconium, et que le phosphate de calcium est présent sous forme de particules dans ladite matrice, lesdites particules ayant une granulométrie maximale de 30 µm.

6. Matériau selon la revendication 4, caractérisé en ce qu'il a une matrice qui comprend essentiellement de l'oxyde d'aluminium, et que le phosphate de calcium est présent sous forme de particules dans ladite matrice, lesdites particules ayant une granulométrie maximale de 15 µm.

7. Matériau selon la revendication 4, caractérisé en ce qu'il a une matrice qui comprend essentiellement de l'oxyde de titane, et que le phosphate de calcium est présent sous forme de particules dans ladite matrice, lesdites particules ayant une granulométrie maximale de 10 µm.

8. Objet qui n'est que partiellement constitué d'un matériau selon l'une quelconque des revendications 4 à 7, lequel matériau forme l'une de plusieurs parties dudit objet, caractérisé en ce qu'une ou plusieurs autres parties dudit objet sont essentiellement constituées d'un ou plusieurs des oxydes dioxyde de titane (TiO_2), oxyde de zirconium (ZrO_2) et oxyde d'aluminium (Al_2O_3).

Fig. 1.

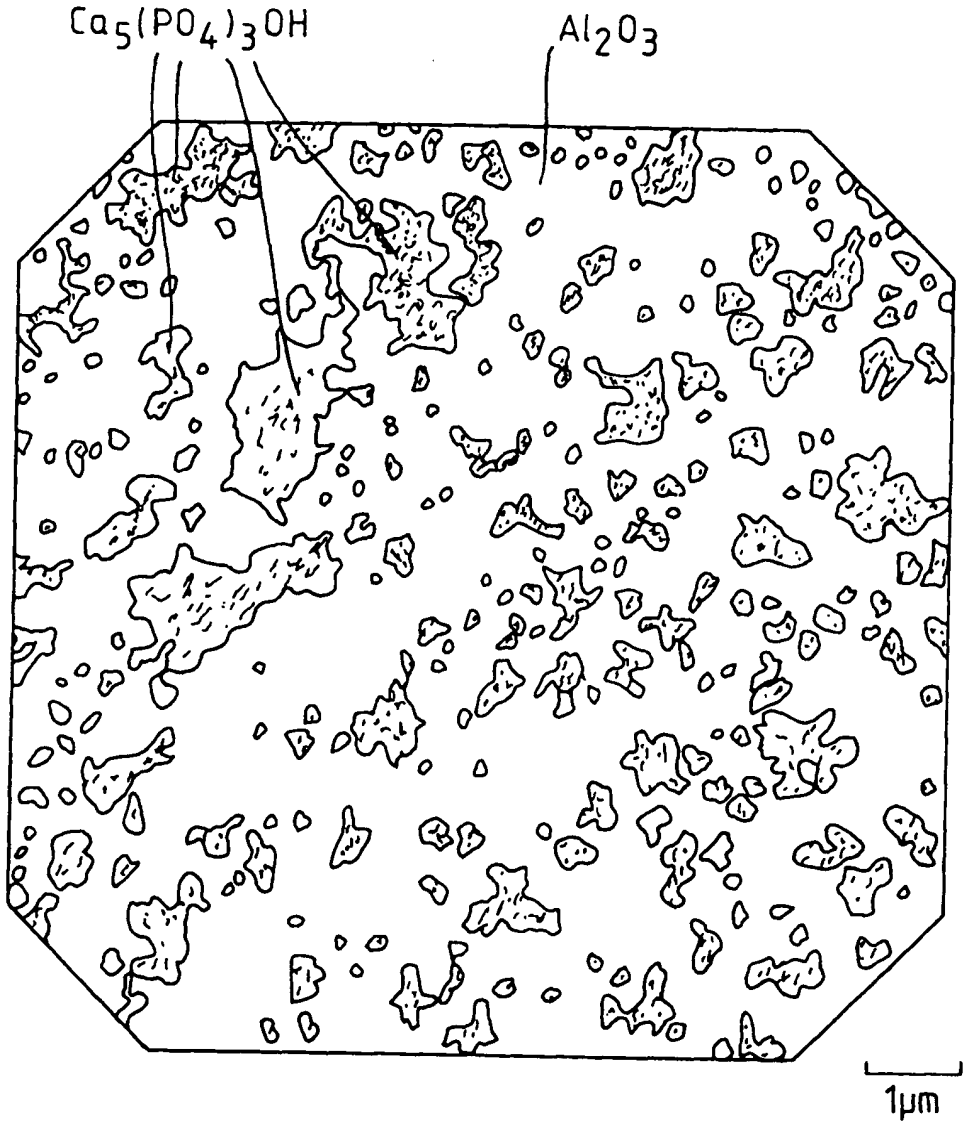

Fig.2.

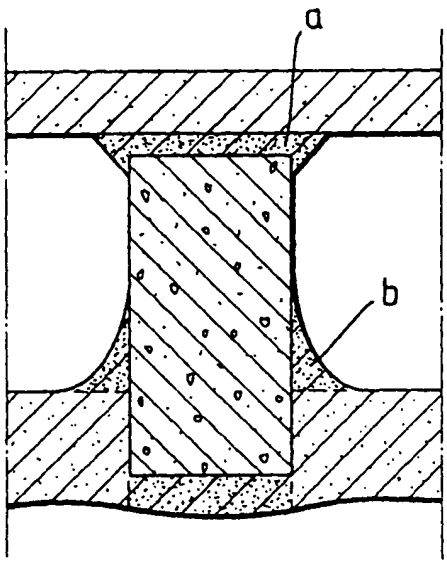

Fig.3.

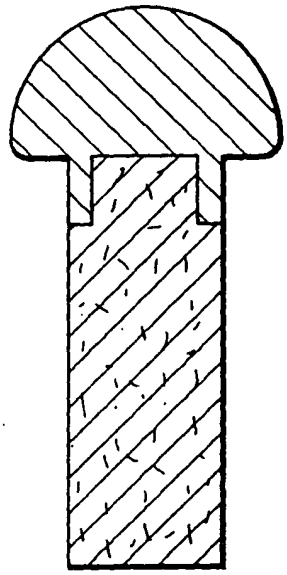

Fig.4.

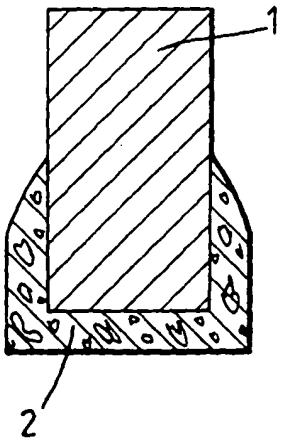

Fig.5.